

**Condensed-Phase Low Temperature Heterogeneous
Hydrogenation of CO₂ to Methanol**

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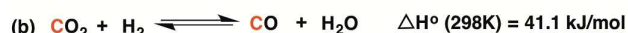
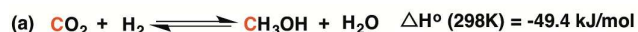
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A low-temperature CH₃OH synthesis was achieved at 120–170 °C using tertiary amine and alcohol in the presence of Cu/ZnO/Al₂O₃ catalyst by CO₂ hydrogenation. A series of 1°, 2° and 3° amines and alcohols were screened to study its influence on the formation of CH₃OH. Particularly, 3° amines such as NEt₃ in combination with EtOH formed CH₃OH with 100% yield with respect to the amine. Unlike the traditional gas-phase heterogeneous metal catalyzed CO₂-to-CH₃OH reactions, no CO is used in the feed gas mixture in this method. In addition, the hydrogenation gives good selectivity (>95%) for CH₃OH and only trace amounts of CO and CH₄ are formed. The presence of CO in the gas mixture was attributed to the decomposition of CH₃OH product, which was confirmed by high-temperature and high-pressure MAS NMR. The reaction was performed in the condensed phase at relatively lower temperature, thus the RWGS reaction, which typically operates at >250 °C, was significantly reduced at this temperature (120–170 °C). The first *in situ* spectroscopic evidence for the condensed phase hydrogenation of alkylcarbonate to CH₃OH via ammonium formate and alkylformate intermediates was also presented under the experimental conditions.

Introduction

Anthropogenic CO₂ emissions into the atmosphere are increasing continuously and it has been widely accepted as a primary cause of global warming and climate change.¹ Similar to the nature's photosynthesis, where the CO₂ is used to construct complex carbon frameworks to store energy harvested from the sunlight, which eventually turned into fossil fuels in million years, a man-made carbon cycle based on CO₂ was proposed by Olah et al.² In the proposed cycle, the CO₂ captured from air or concentrated sources are converted to chemicals and fuels in short time. CO₂ is an inexpensive and abundant C₁ building block. Industrially, CO₂ is already used to manufacture urea, salicylic acid, cyclic carbonate and polycarbonate.³ In addition, hydrogenation of CO₂ can produce various chemicals such as, CH₃OH, CH₄, HCO₂H, HCOOCH₃, depending on the catalyst and the reaction conditions.⁴ Among these CO₂ hydrogenated products, CH₃OH contains high hydrogen weight content (12.5 wt%) and it is also a basic commodity chemical for the synthesis of aromatics, olefins (ethylene and propylene), high-octane gasoline and other chemicals.⁵ Current industrial CH₃OH synthesis is based on a Cu/ZnO/Al₂O₃ heterogeneous catalyst that utilizes a CO₂/CO and H₂ mixture, which operates at high temperatures (250–300 °C) under high pressures (7 Mpa–10 MPa).⁶

Since the CH₃OH formation step is exothermic, low temperature and high pressure favor the selective formation of CH₃OH (Scheme 1). Typically, higher temperatures are required for the hydrogenation of CO₂ to CH₃OH using heterogeneous catalysts.^{8a} Higher temperature favors the reverse water gas shift (RWGS) reaction and produces CO, which significantly reduces the CH₃OH yield with respect to CO₂ and it also consumes valuable H₂. The CO and H₂O formed from the RWGS reaction is known to have detrimental effect on the Cu/ZnO/Al₂O₃.⁷ Therefore, in order to reduce the production costs and also to utilize the exothermicity of the CO₂-to-CH₃OH reaction, it is desirable to perform the reaction at lower temperature.



Scheme 1. CH₃OH formation and RWGS from CO₂ hydrogenation.

The formation of CH₃OH from CO₂ proceeds via formate (HCOO_{ad}), acetal (OCH₂O_{ad}) and methoxy (OCH_{3ad}) intermediates.⁸ Irrespective of CO₂/H₂ or CO/CO₂/H₂ reaction systems, formate is always the reaction intermediate for the CH₃OH synthesis, and the hydrogenation of formate was identified as a rate-limiting step.⁹ In 1995, Noyori et al reported that the addition of alcohol and base promote the homogenous hydrogenation of CO₂ to formate.¹⁰ Similarly, several systems were reported for the homogenous metal catalyzed formate and CH₃OH synthesis from CO₂ in the presence of alcohols and bases.¹¹ We note that alcohols and bases promote this reaction as both reagents produce dissolved anionic carboxylates (carbamates and/or alkylcarbonates) from CO₂,¹² which are electrophilic enough to be reduced by catalysts via an inner sphere mechanism.^{12b}

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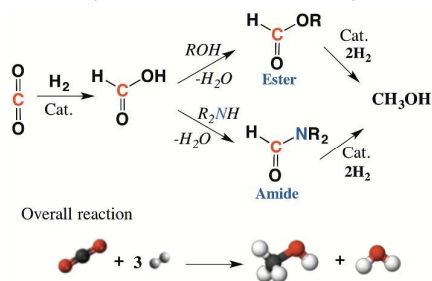
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Formate salts can then undergo thermal condensation to either a formate ester (in the presence of alcohol) or formamide (in the presence of amine), which subsequently get hydrogenated to CH₃OH (**Scheme 2**). We note that literature reports cite the need for Lewis acid or base to drive the hydrogenation of formate esters and formamides to CH₃OH by homogeneous catalysis.¹¹ We hypothesized that the reactive pathways demonstrated through homogeneous catalysts would be available to heterogeneous catalysts, as the hydrogenations to CH₃OH have been shown to be catalytic with respect to capture solvent (amine and/or alcohol). Furthermore, the solid-support of heterogeneous catalysts could provide Lewis acid/base sites required for the final hydrogenation of formate esters or formamides to CH₃OH.¹³ The effect of amine and/or alcohol additives on the productivity of the CH₃OH synthesis catalyst was studied previously using heterogeneous catalysts by different groups.¹⁴ However, most systems reported so far present series of challenges, namely use of CO in the feed gas mixture, require to start from alkylformate ester, stop at alkylformate ester intermediate, undergo decomposition of amines employed, and show low activity/selectivity for CH₃OH, which is still a major challenge. In order to address these challenges, careful study of reaction pathways is necessary to design a versatile and robust system for CH₃OH production from CO₂ at low-temperatures with high selectivity/activity.

Herein, we report a lower-temperature condensed phase heterogeneous hydrogenation of CO₂ to CH₃OH using only CO₂ as a C₁ source using the commercial Cu/ZnO/Al₂O₃ catalyst at 170 °C under 60 bar CO₂: H₂. We utilized both base (amine) and alcohol to promote the formation of CH₃OH at low-temperature via formamide or formate ester intermediates in the condensed-phase. Thereby we significantly reduced the RWGS reaction and established a new approach for the heterogeneous metal catalyzed CO₂ hydrogenation at low temperature employing inexpensive NEt₃ and EtOH as additives. *Operando* ¹³C NMR spectroscopy of this reaction demonstrates the reaction proceed via alkylcarbonate, formate, and formate ester intermediates.

Results and Discussion

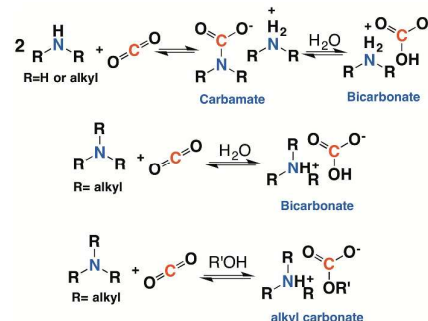
CO₂ can be captured from air or concentrated sources by amine, amine/H₂O, or amine/alcohol mixture to form carbamate, bicarbonate and carbonate respectively (**Scheme 3**).¹⁵ The CO₂ activated by this fashion can either be directly used or it can be released by temperature and/or pressure swing, then compressed and concentrated to produce useful CO₂-derived products.



Scheme 2. Proposed pathways for the CO₂ hydrogenation to CH₃OH.

In this study, we subjected the *in-situ* formed carbonates and carbamates to hydrogenation. Bicarbonates are not chosen for this study because the presence of H₂O is known to poison the

Cu/ZnO/Al₂O₃ catalyst.^{16,14h} We initially screened 1° and 2° amines, finding that amine bases were hydrogenated to their respective formamides, but were unable to continue to CH₃OH (entry 1 and 2, **Table S1**). This result indicates that the formamide route (**Scheme 2**, bottom) may not be feasible under these conditions, which we attribute to the low hydride acceptor strength (low electrophilicity) of formamides compared to that of formate esters.



Scheme 3. CO₂ capture using different amines.

Tertiary amines (NEt₃) were found to be non-reactive, as were alcohol (EtOH), though the combination of 3° amine and alcohol produced CH₃OH (entry 1-3, **Table 1**). These results suggest that the neutral CO₂ may not be the active species. Thus, we propose that the anionic alkyl carbonate is possibly the active species likely via

Table 1. Hydrogenation of CO₂ to CH₃OH

Entry	Promoters	Amine: alcohol	HCOO ⁻	HCOOEt	CH ₃ OH
1	NEt ₃	-	trace	-	-
2	EtOH	-	-	-	-
3	NEt ₃ : EtOH	1:1	trace	trace	2%
4	NEt ₃ : EtOH	10:1	-	-	-
5	NEt ₃ : EtOH	1:10	3%	trace	100%
6 ^a	NEt ₃ : EtOH	1:10	3%	1%	76%
7 ^b	NEt ₃ : EtOH	1:10	-	1%	28%
8 ^c	NEt ₃ : EtOH	1:10	4%	4%	19%
9	NEt ₃ : EtOH	1:5	trace	trace	7%
10	TMEA:EtOH	1:10	-	1%	18%
11	DEEA:EtOH	1:10	0.5%	trace	21%

Standard reaction conditions: Catalyst=Cu/ZnO/Al₂O₃ (300 mg), CO₂/H₂=60 bar (1:2), EtOH (200 mmol), amine (20 mmol), T=170 °C t=16h. HCOO⁻, HCOOEt and CH₃OH yield are based on ¹H NMR. The yields are calculated with respect to the amine. ^a40h, ^b150°C and ^c120°C

the observed coordination to the cationic metal surface by which hydrogenation to HCO₂H occurs, *vide infra*. The methanol conversion is reported against the amount of amine as it provides a readily available internal standard to calculate against. NEt₃ and EtOH produced CH₃OH at 2% conversion with respect to NEt₃ (entry 3, **Table 1**). While the tertiary alkanolamines, N,N,N',N'-tetrakis(2-hydroxyethyl) ethylenediamine (THEED) and triethanolamine (TEA) decomposed at high temperature (entry 4 and 5, **Table S1**). Diethylethanolamine (DEEA) however, produced 6.5 mmol of CH₃OH (4% conversion based on amine, entry 6, **Table S1**). Unexpectedly, Proton-sponge and Bisphenol A underwent partial hydrogenation of aromatic ring (entry 7 and 8, **Table S1**) and were not tested further.

Changing the ratio of amine to alcohol influenced the conversion to CH₃OH; if the ratio of amine to alcohol was 10:1, the conversion of CH₃OH with respect to amine is poor, whereas a ratio of 1:10 enables a 100% conversion to CH₃OH with respect to amine (entry 4 and 5, **Table 1**). The CH₃OH synthesis activity as high as 4166 mmol/(Kg-cat-h) was obtained at 170 °C with a CH₃OH yield of ~10% with respect to CO₂. An excess of NEt₃ could passivate the catalyst surface and limiting the reaction. It is likely that polarity has a strong influence on the reactivity as we have shown the formation of alkylcarbonates to be highly sensitive with respect to polarity.^{15a} The relatively lower polarity of NEt₃ would disfavor the formation of the highly polar alkylcarbonate, whereas an excess of alcohol would be polar enough to favor alkylcarbonate formation. Further EtOH could solvate polar transition states and charged intermediates common to CO₂ hydrogenations whereas NEt₃ would not. Excess alcohol would also promote the thermal esterification to produce formate ester. Gas chromatographic analysis of the gas mixtures only showed trace of CH₄ and CO in addition to excess H₂ and CO₂.

Table 2. Effect of basicity of amine on the carbonate formation

Entry	Amine	pKa	Methyl carbonate (%)	IR (CO) cm ⁻¹	¹³ C NMR (ppm)	
					I ^a	II ^b
1	DBU	12	98	1642	52.2	159.8
2	DIPEA	11.4	92	1647	51.1	158.8
3	NEt ₃	10.6	75	1654	52.3	160.1
4	DMAP	9.9	64	1651	52.4	160.5
5	DABCO	8.8	64	1650	49.1	160.0
6	Pyridine	5.5			No reaction	

Standard reaction conditions: (A) alkylcarbonate formation from CO₂ capture –alkylcarbonate yield calculated with respect to amine by ¹³C NMR of 2M amine in CH₃OH under 10 bar CO₂ at RT, ^aNMR resonance of methyl carbon in CH₃OCCO⁻ species, ^bNMR resonance of carbonate carbon in CH₃OCCO⁻ species. DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene, DIPEA = N,N-Diisopropylethylamine, DMAP = 4-Dimethylaminopyridine, DABCO = 1,4-diazabicyclo[2.2.2]octane

The necessity for the combination of non-nucleophilic bases and alcohols suggests CH₃OH production proceeds via the formate and formate ester route (**Scheme 2**). The presence of amine and alcohol promotes the formation of alkylcarbonate, ammonium formate and alkyl formate ester intermediates. Under optimal conditions, the amount of CH₃OH produced never surpassed the amount of amine used regardless of time, which is suggestive of an established equilibrium (entry 6, **Table 1**). Even at lower temperatures 150 °C and 120 °C, moderate CH₃OH yields were obtained (entry 7 and 8, **Table 1**) suggesting that the reaction does not necessarily need to proceed at 170 °C. Tetramethylethylenediamine (TMEA) and DEEA formed 18% and 21% CH₃OH respectively in presence of excess EtOH (entry 10 and 11, table 1). From entry 11, **Table 1** and entry 6, **Table S1**, it is clear that the presence of excess alcohol does not improve the amount of CH₃OH formed in the case of DEEA base as it decomposes under these conditions.

We then studied the effect of basicity on alkylcarbonate formation capacity of the amines and alcohols on the CH₃OH formation. The alkylcarbonate formation in **Table 2** was studied under high pressure since some alkylcarbonates are not stable under atmospheric conditions. From **Table 2**, it is clear that the strong bases give high methyl carbonate yield, however with low

CH₃OH yield (**Figure 1**). While less basic amines give moderate methyl carbonate yield but high CH₃OH yield. NEt₃ showed the highest CH₃OH yield, suggesting a pKa of the conjugate acid above or below 11 (in H₂O) is optimal under these conditions. Since aromatic ring hydrogenation was observed in the presence of Cu/ZnO/Al₂O₃ catalyst (*vide supra*), DMAP and pyridine were not chosen for the CO₂ hydrogenation study.

Table 3. Effect of alkyl chain length and sterics of alcohol on the

Entry	Alcohol (%)	pKa	Alkyl carbonate (%)
1	CH ₃ OH	16	75
2	EtOH	15.9	75
3	<i>i</i> -propanol	16.5	25
4	Ethylene glycol ^a	14.2	35
5	<i>t</i> -Butanol	17	No reaction
6	Phenol ^b	10	No reaction

carbonate formation

Standard reaction conditions: Alkylcarbonate formation from CO₂ capture –alkylcarbonate yield calculated with respect to amine by ¹³C NMR of 2M NEt₃ in alcohol under 10 bar CO₂ at RT, ^aOnly one OH group is carbonated. ^bthe reaction was performed in THF.

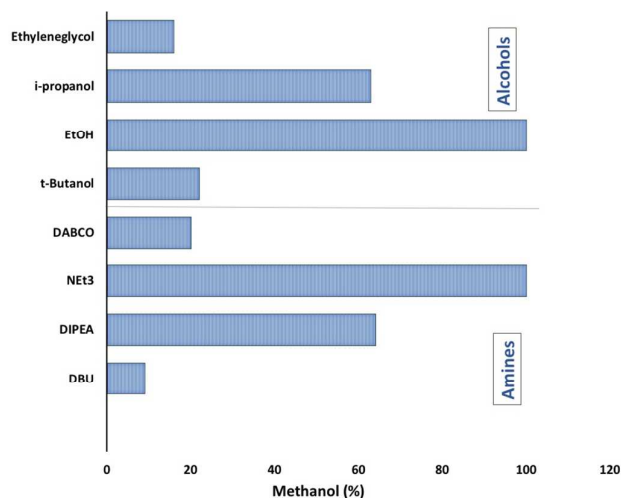
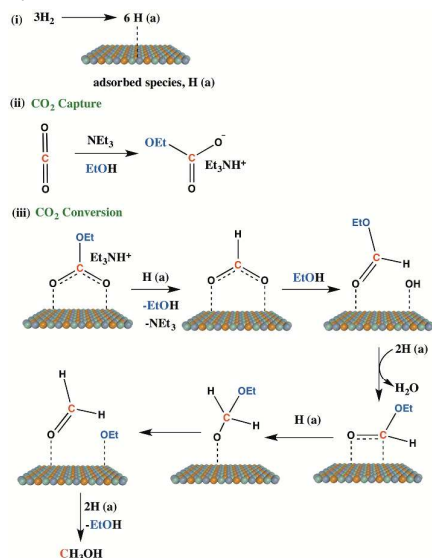


Figure 1. Standard reaction conditions: (A) Alcohols: catalyst=Cu/ZnO/Al₂O₃ (300 mg), CO₂/H₂=50 bar (1:2), EtOH (200 mmol), amine (20 mmol), T=170 °C, t=16h, (B) Amines: catalyst=Cu/ZnO/Al₂O₃ (300 mg), CO₂/H₂=50 bar (1:2), alcohol (200 mmol), NEt₃ (20 mmol), T=170 °C, t=16h, CH₃OH yield calculated with respect to amine.

Similarly, the choice of alcohol on the alkylcarbonate was investigated under pressure (**Table 3**). The presence of CH₃OH or EtOH did not show significant difference in the alkylcarbonate yield, which is contributed to similar pKa's of the alcohols. However, the alkyl chain length and sterics significantly reduced the alkylcarbonate conversion and CH₃OH yields (**Figure 1**). This result is consistent with our previous observations that secondary alcohols do not form as much alkylcarbonate as linear alcohols because of steric crowding.¹⁷ Similarly, phenol is likely not electrophilic enough to attack CO₂ and doesn't carboxylate under these conditions (entry

6, Table 3). The results obtained from Table 2, Table 3 and Figure 1 suggests that the 3° amines and short linear alcohols are the best combination for high CH₃OH yield, consistent with conditions that favor alkylcarbonate formation.



Scheme 4. Plausible reaction mechanism for the one-pot CO₂ capture and conversion.

While a direct correlation between the alkylcarbonate formed and CH₃OH formation was observed (Table 2 and Table 3), it is expected that there is a small amount of alkylcarbonate present at 170 °C under 25 bar CO₂. Based on our observations and the literature studies¹⁸, we propose a plausible reaction mechanism via coordination of anionic ethyl carbonate to the catalyst surface, by which the reaction proceeds via formate and ethylformate intermediates (Scheme 4). Catalyst recycling was studied under 1:2 CO₂:H₂ pressure. In the second run, some drop in catalytic activity was observed. However, the activity remained the same in the third run. The decrease in the catalytic activity was probably due to the catalyst sintering, which was confirmed by powder X-ray diffraction (XRD) - performed after the third run (Scheme S7). The Cu particle size increased from 21 nm (freshly reduced) to 40 nm (spent). Similar sintering of catalyst in the batch reactor was observed previously in the presence of H₂O, the byproduct.⁷ XRD analysis also showed the presence of ZnCO₃, which could have formed from an excess CO₂ concentration under pressurized conditions.¹⁹ Thus, changes in activity could be explained by both sintering of the Cu particles and due to phase change of the ZnO support. However, at this point of the study, it is not clear whether ZnCO₃ is involved in the active catalytic cycle. We note that inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis of the solution after the hydrogenation showed minimal catalyst leaching (Cu=2.2 ppm, Zn=5.1 ppm, Al=<1.3 ppm)."

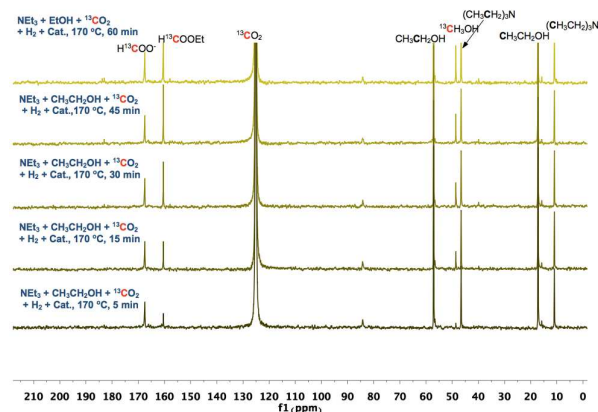


Figure 2. *In-situ* ¹³C MAS NMR of the reaction mixture (NEt₃:10EtOH, ¹³CO₂ and H₂) in the presence of Cu/ZnO/Al₂O₃ at 170 °C, 1h.

High temperature *operando* ¹³C magic angle spinning (MAS) NMR study of the catalyst in the presence of 1:10 NEt₃ and EtOH mixture at 20 bar of CO₂ at 120 °C showed ethylcarbonate (158.9 ppm) at a concentration 2.2 times that of the active sites on the catalyst. We also observed ethylcarbonate bound to the catalyst (165.7 ppm) at a concentration that is 22% of the active site calculated for the catalyst (Figure S2). 19% conversion to CH₃OH was observed at 120 °C (Table 1) indicating ethylcarbonate exists in a significant enough concentration to participate in the reaction at least up to this temperature.

Operando ¹³C MAS NMR at 170 °C in the presence of H₂ did not show a detectable amount of ethylcarbonate, though it clearly showed the formation of triethylammonium formate (168.5 ppm) as an initial intermediate, which then converted to ethyl formate (161.2 ppm). CH₃OH signal at 48.7 ppm started to grow quickly in less than 5 min of heating at 170 °C (Figure 2). Over time CH₃OH decomposed into CO (182.2 ppm), confirming the hydrogenation does not proceed via CO.

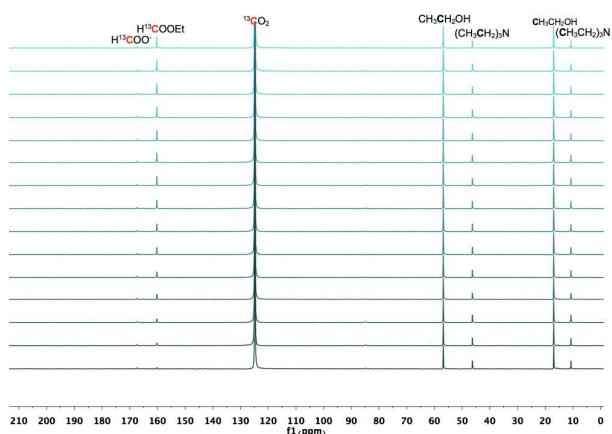


Figure 3. *In-situ* ¹³C MAS NMR of the reaction mixture (NEt₃:10EtOH, ¹³CO₂ and H₂) in the presence of Pd/ZnO at 170 °C, 15h.

We also studied the CO₂ hydrogenation via the ammonium formate and alkyl ester intermediates in the presence of Pd/ZnO catalyst under the same conditions studied previously for the Cu/ZnO/Al₂O₃ catalyst. Though Pd/ZnO was well-studied in the

literature for CH₃OH formation via CO route (>250 °C),²⁰ there was no detectable amount of CH₃OH observed by ¹³C NMR at 170 °C. However, slow accumulation of alkyl formate was observed overtime (Figure 3).

Conclusions

We have demonstrated a low-temperature condensed phase heterogeneous hydrogenation of CO₂ to CH₃OH using NEt₃ and EtOH. The formation of side products such as CO and CH₄ are significantly reduced. Screening of various amines and alcohols revealed that the alkyl carbonate, ammonium formate and alkyl ester are the key intermediates involved in the reaction which was confirmed by *Operando* ¹³C MAS NMR. The degree of alkyl carbonate and methanol formation were found to be limited by polarity of solvents as well as basicity of the amine. Performing the present reaction in a flow system could significantly improve the overall productivity of the system, as poisoning of catalyst arising from the accumulation of products would be minimal.

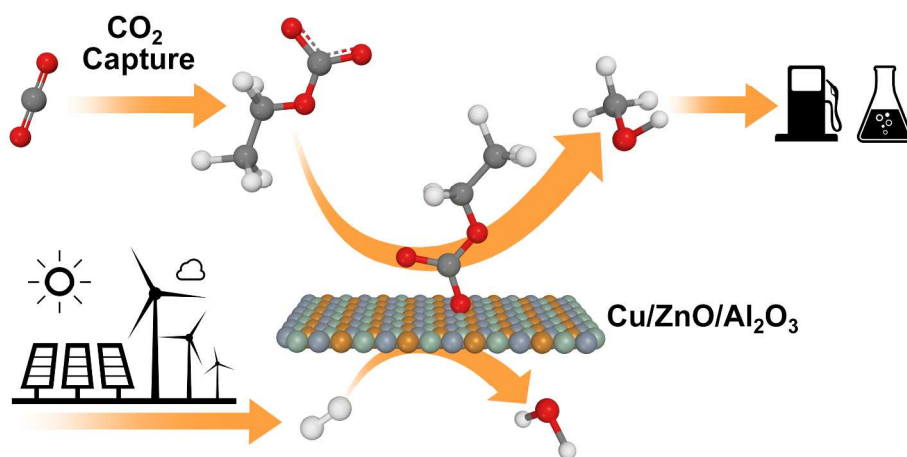
Acknowledgements

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